NOVEL POLYBUTADIENE DERIVATIVE CURABLE WITH IONIZING RADIATION

DETAILED EXPLANATION OF THE INVENTION

The present invention relates to a process for preparing a novel radiation-curing polymeric compound, which substantially comprises reacting a butadiene homopolymer, a butadiene copolymer or a mixture thereof which have functional groups containing active hydrogen in its molecule, with an isocyanate compound having substituted or unsubstituted vinyl group. The principal objects of the present invention are; (1) to provide resin materials with high flexibility, which is susceptible to radiation, that is, which is curable with the irradiation of low radiation dose, (2) to provide a raw materials for paint composition which results in the painted films having excellent flexibility, shock resistance and adhesive properties, and (3) to provide raw materials for use as bonding agents with excellent adhesive strength at high temperature. Moreover, the applications as raw materials in resin-fiber composites, as fiber conditioning agents, artificial leather and the like are contemplated.

It has been known that thermo-setting resin, film forming paint material, bonding agents and the like can be produced by polymerizing a butadiene polymer having a molecular weight of 200 – 100,000 under heating in the presence of curing agent such as an organic peroxide and various curing accelerators. However, in the production of cured resin produced from such butadiene polymer as raw material, the working propery property quite low and industrial mass production is difficult or impossible, because the heat curing requires a temperature above 150°C for a long period ranging to several days, and from more than several hours even with use of a curing accelerator. Furthermore, such processes have the disadvantages in that the pot life is limited when a curing agent comprising organic peroxide or curing accelerator is mixed with the polymer, and the cured resin has poor flexiblity and is occasionally cracked.

Moreover, the application of such paint composition prepared from butadiene polymer has been restricted to the materials which withstand heating, and the application to wood board, plywood, plastics, fiber or the like has been considered to be impossible. The painted film has poor shock resistance and poor adhesive properties, and the bounding agent has poor adhesion to metallic material.

As the result of the many studies involving the methods of preparing resins, paint compositions and bonding agents in which butadiene polymers are used as raw materials seeking to improve the properties of such products; the present inventors have achieved the present invention by discovering that the disadvantages mentioned above are considerably improved when a novel polybutadiene derivative, which is obtained by the reaction of an isocyanate compound containing substituted or unsubstituted vinyl groups with a butadiene polymer which has functional groups containing active hydrogen, is used as raw material for radiation-curing resin, and that it is possible to provide curable resins, paint compositions and bonding agents with high flexibility which are curable at room temperature in a short period of time without addition of curing agent such as organic peroxide or various kinds of curing accerelators.

The present invention is explained below more concretely. The invention relates to a method of preparing novel radiation-curing polybutadiene derivatives, in which butadiene homopolymers, butadiene copolymers or their mixtures having the number-average molecular weight of approximately 200 – 100,000, having more than about 30% of butadiene unit of 1.2-bond in its polymerized chain and having functional groups containing active hydrogen (these polymers are defined hereinafter as "butadiene polymer containing active hydrogen"), are allowed to react with an isocyanate compound having substituted or unsubstituted vinyl group (these compounds are defined hereinafter as "isocyanate compounds containing substituted or unsubstituted vinyl group") in the ratio of more than about 0.5 equivalent, preferably 0.8 – 1.2 equivalent, of isocyanate groups in the latter to one equivalent of active hydrogen in the former. The order of the processes to produce the above mentioned derivatives in the present invention is not restricted, therefore, changes and modifications of the reaction processes, in which, for instance, an isocyanate compound without a vinyl group is allowed to react with a butadiene polymer to form the derivative at the beginning and subsequently the vinyl group is introduced into the derivative, fall under the present invention as a matter of course.

The analysis of the mechanism for the unexpected excellent effect by introducing above mentioned each functional group into the novel radiation-curing polybutadiene derivatives in the present invention is in progress, whereas it is understood that reasonable flexibility, adhesiveness and luster are given to resins, paint compositions and bonding agents by urethane-, urea-, amide-bond and the like which result from the reaction between the functional group containing active hydrogen in the butadiene polymers and the isocyanate group, and furthermore the reactivity (curable ability by irradiation) of the derivative is increased by the presence of the vinyl group in the isocyanate compound, consequently advantageous effects, that is, reduction of the radiation dose required for curing, increase in the hardness of the painted film and the like are achieved. Moreover, the coexistence of the above effects is a requisite condition to attain the expected objects. Butadiene polymer having 1.2-bond, moreover, contains pendant reactive vinyl groups in its molecular structure, whereas it is considered that the unsubstituted or substituted vinyl groups in the isocyanate compounds are more reactive than the pendant vinyl groups mentioned above and result in a synergystic effect in which the intermolecular cross-linking reaction is effectively carried out during the process of radiation curing, particularly at the initial stage of the process. Particularly, the effect tends to be more considerable when an electrophilic group such as carbonyl group is bonded to the α-carbon to which vinyl group is attached.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The butadiene polymer containing active hydrogen used in the present invention means the butadiene polymer with number-average molecular weight of 200 – 100,000, butadiene copolymers containing butadiene units of more than about 50 percent, and their mixtures, the butadiene polymer containing active hydrogen such as provided by hydroxyl-, carboxyl-, mercap-